A Literature Survey of Noble Gas Solubility Measurements in Formation Brines to Interpret Tracer Experiments

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By

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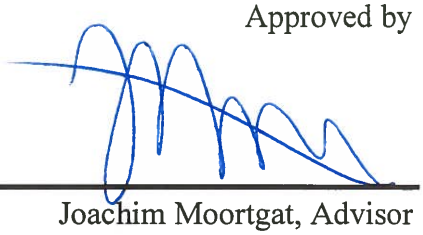

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ABSTRACT

Subterranean fluid compounds of interest in the Earth's crust, such as natural gas, oil, asphalt, condensate, brine, and freshwater are obscured from direct observation. Even with modernizations of technology and science, fluid behavior in the sub-surface remains a mystery. Understanding the fluid interactions that are normally obscured from direct observation, has been accomplished with "tracer" elements and compounds. These compounds are usually inert to decay or reaction in order to preserve distinguishable characteristics. Due to the unique radio-nucleic composition and relative abundances, the noble gases are particularly powerful natural fluid tracers. Determining expected patterns in a fluid mixture requires knowledge of solubility to interpret physical processes. The noble gas solubilities have been described by the Ideal Gas Equation of state (EOS), Peng-Robinson EOS, and Redlich-Kwong EOS. Yet, all have caveats and nuances. This work makes the steps toward empirical based explanation through examination of eleven published works in the literature of aqueous noble gas solubility. Utilizing this dataset, interpretations of solubility patterns using temperature and pressure are then made. Empirical datasets such as these can provide a measure of validation for theoretical equations and models to provide a means to better interpret and predict the effects of fluid flow phenomena underground.

ACKNOWLEDGEMENTS

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INTRODUCTION

Fluid modeling of subsurface reservoirs is a chief point of interest in the oil and energy industries. Fluid flow affects the geographic location, composition, and economic viability of a petroleum resource. Developing an understanding of how fluids behave in subsurface conditions is therefore of utmost importance. The Noble gases are nearly chemically inert and originate from either radioactive processes (Ballentine & Burnard 2002) or primordial gases contained in the accretionary process during the formation of Earth. These distinct sources form a pattern, or fingerprint in relations of mass abundance and isotope ratios. These composition patters have become markedly different for the atmosphere, crust, and mantle over the course of earth history due to natural partitioning in the fluid systems. As fluids are exchanged between the Earth's layers and systems, the noble gases remain chemically unaltered, creating a record that could be read to reveal the fluid mechanic history for a reservoir body of interest (Ballentine et. al. 2002).

Several models to describe these fluid systems exist, however under severe limiting assumptions. As an example, the Lewis-Randall rule of fluid mixing only applies if it is assumed that unlike molecules do not affect one another (Ballentine et. al. 2002), however it is well-know that this assumption breaks down for some of the noble gases under elevated temperatures and pressures (i.e., at depth). More generally, noble gases at surface conditions can be described by the Ideal Gas equation of state (EOS), but when dissolving in hydrocarbon or aqueous fluids at subsurface temperatures and pressures, more complex equations of state are required to describe their phase behavior (Abudour et al. 2014). Such equations of state require experimental data over the range of temperatures and pressures of interest to tune a number of adjustable parameters.

To the best of my knowledge, such EOS modeling has not been demonstrated in the literature. As a first step towards this goal, this work compiles literature data on the solubilities of ^{4}He, ^{20}Ne, ^{40}Ar, ^{84}Kr, and ^{132}Xe noble gases in water for temperatures between 288.15K and 557.35K and pressures ranging from 1atm to 95.84atm.

GEOLOGIC SETTING

Freshwater Aquifers

Noble gas concentrations in near surface bodies of waters are primarily a property of equilibration between the solvent system and atmospheric gas (Aeschbach-Hertig et. al. 1999). The nature of these dissolved gases once the water infiltrates into underground aquifers is less clearly understood. Water that has equilibrated with the atmosphere may migrate downwards due to buoyancy and hydraulic conductivity factors, and thus interact with trapped reservoir waters (Heilweil et. al. 2004). Residual connate waters left in formation after interaction have distinct concentrations of dissolved gases. Interpretations from the abundancies of the dissolved noble gases in these waters may include initial equilibration temperatures, useful in recreating paleo-climate and paleo-temperature scenarios. (Aeschbach-Hertig et. al. 1999)

Oil Reservoirs

Petroleum resources, while not the only subterranean fluid commodity are often the most valuable, and therefore are highly sought after. Kerogen is chemically broken down and converted to lighter hydrocarbon fluids and gases in the "oil window" conditions of between 50ºC and 150ºC with elevated, if somewhat variable, pressure (Tissot & Welte 1984). These fluids do not always remain static (Wang et. al. 2017). A significant amount of evidence is present to suggest migration from source rock to reservoir structures and formations (Wilson 2005). By modeling hydrocarbon migration by evaluation of noble gas abundances it is possible to interpret multi-phase and multi-component systems, fluid saturations, and paleo-interactions. (Tang & Harker 1999)

Figure 1 illustrates some of the various processes and interactions that lead to noble gas accumulation, transfer, and mixture in oil and water reservoirs. For example, meteoric water from the atmosphere may seep into the crust, as well formation waters can be over-pressured to a potentiometric level above the ground surface. Thereby exchange between atmospheric and crustal systems is facilitated. This interaction, while not the only such exchange, accounts for a bulk of the petroleum reservoir system interactions (Kipfer et. al. 2002).

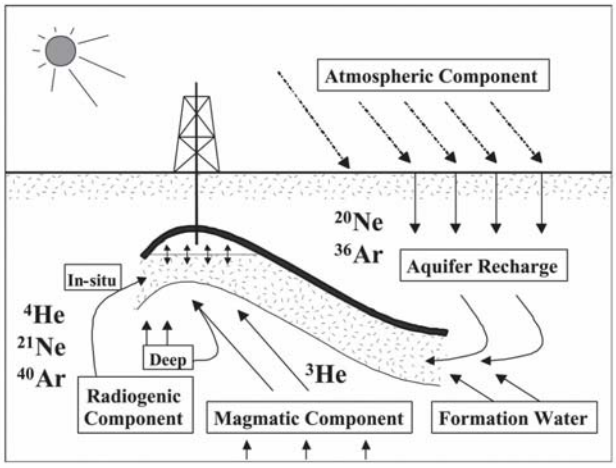

Figure 1: (Figure and caption taken from Ballentine et. al. 2002) Schematic diagram of a gas reservoir, illustrating the different noble gas components which may occur in crustal fluids. Atmosphere-derived noble gases (e.g., ^{20}Ne and ^{36}Ar) are input into the gas phase on equilibration with the groundwater system containing dissolved atmosphere derived noble gases. Radiogenic noble gases (e.g., ^{4}He, ^{21}Ne and ^{40}Ar) are produced by the natural decay of the radioelements U, Th and K in the crust, and are also incorporated into crustal fluids. Within areas of continental extension or magmatic activity, noble gases derived from the mantle (e.g., ^{3}He) may also be present in crustal fluids. The distinct isotopic and elemental composition of these different noble gas components allows the extent of their contribution to any crustal fluid to be quantitatively resolved and information about volumes, source and transport process of associated fluids to be identified.

METHODS

Experimental setup

Figure 2 displays the apparatus Crovetto et. al. (1981) used to perform measurement of gas solubility by isolating the desired sample from outside influence. The device was able to isolate its internal environment within a stainless steel tube to allow for gas equilibration into solution, whilst pressure and temperature were measured continuously. A large opening at one end allowed for pressure gauges to be connected and monitor conditions, and a small capillary tube at the opposite end serves to extract a sample of the liquid solution to be measured for dissolved gases. Figure 3 illustrates the steel isolation chamber in conjunction with the measurement devices used by Crovetto et. al. (1981)

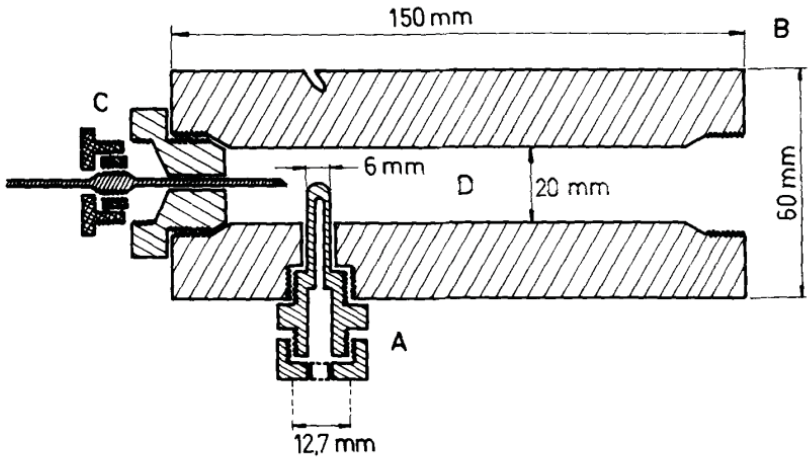

Figure 2: Stainless Steel isolation tube, used by Crovetto et. al (1981): A) Temperature Probe, B) Opening for connection to Bourdon pressure gauges, C) Capillary rube for liquid solution extraction, D) Inner equilibration chamber.

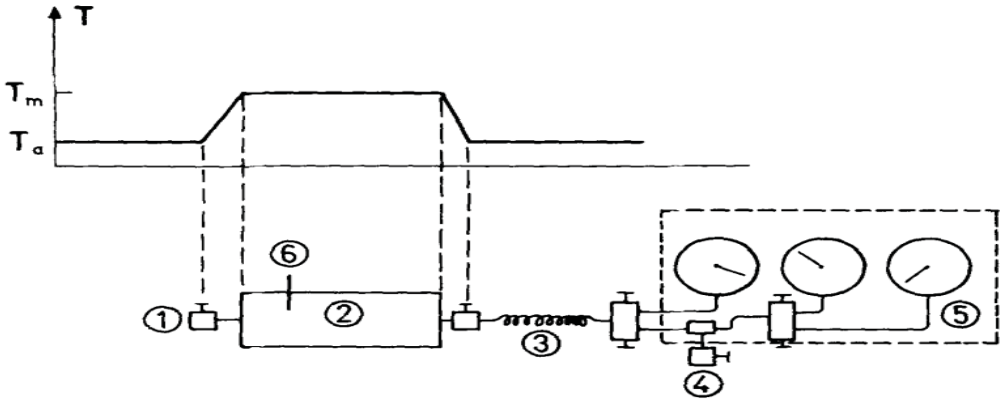

Figure 3: Complete measurement apparatus used by Crovetto to measure noble gas solution solubility. (Taken from Crovetto et. al. 1981)

Experimental setups exploiting examination of the same physical properties using very similar methods to achieve certainty in solution equilibration were used in the experiments by Potter & Clyne (1978), Pray & et. al. (1952), and Stephan et. al. (1956) used to collate Table A.

Conversion: Volumetric Solubility to Mole fraction

Solubility's collected from Pray et. al. (1952) and Stephan et. al. (1956) were originally reported in Volume Solvent(mL)/Mass Solute(g). These values are converted to mole fractions, to compare to molar solubilities in other literature data, using Equation 1. Standardization of data in mole fraction units allows examination and interpretation of the data, without needing to account for density property changes for each data point. These density fluctuations are brought on by temperature or pressure varying away from STP.

$$X(gas) = \frac{dV(gas) \times A}{dV(gas) \times A + 1} \tag{1}$$

Equation 1: Mole Fraction gas [X(gas)] is equivalent to change in volume of gas times factor A (to account for density property changes with temperature and pressure), divided by change in volume of gas times factor A +1

$$A = \left[\frac{\rho(gas)}{\rho(water)}\right] \frac{MW(water)}{(MW(gas))} \tag{2}$$

Equation 2: Factor A, is equivalent to density gas over density water times molecular weight water over molecular weight gas.

Results

Solubility as a function of Temperature

For any reasonable examination or interpretation of noble gas solubility trends to occur, data must be organized to isolate pressure and temperature dependences, the physical variables effecting the solubility. Figure 4 displays data for several Noble gases and methane across a range of temperatures, at a system pressure of 1atm (101.325 kPa).

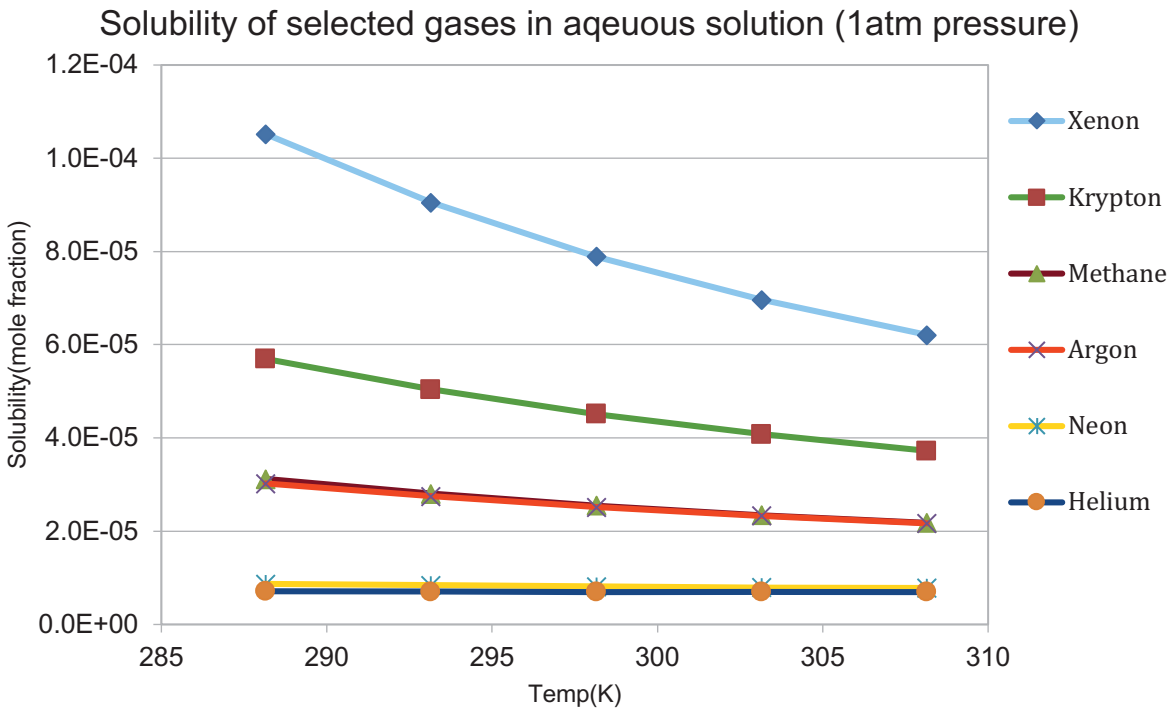

Figure 4: Solubility of He-4, Neon, Argon, Krypton, Xenon, and Methane. Pressure of solution remained constant 1atm. Temperature was ranged 288.15K-3083.15K. The data in represents empirical values derived from IUPAC chemical solubility series, compiled by Crovetto

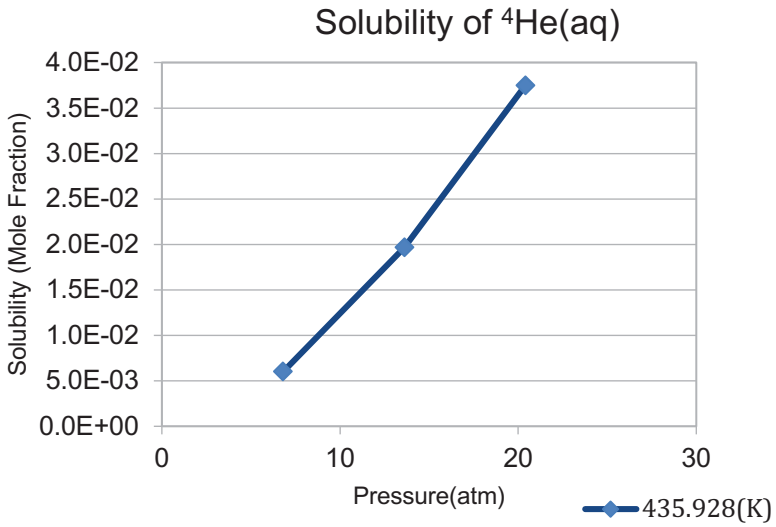

Figure 5: Plot of Helium-4 solubility series at constant temperature

Solubility as a function of pressure

Unfortunately data, from which temperature or pressure trends could be constructed, were sparse. Much of the historical empirical data ranges along increments and condition values specific to that experiment. (Himmelblau 1960)

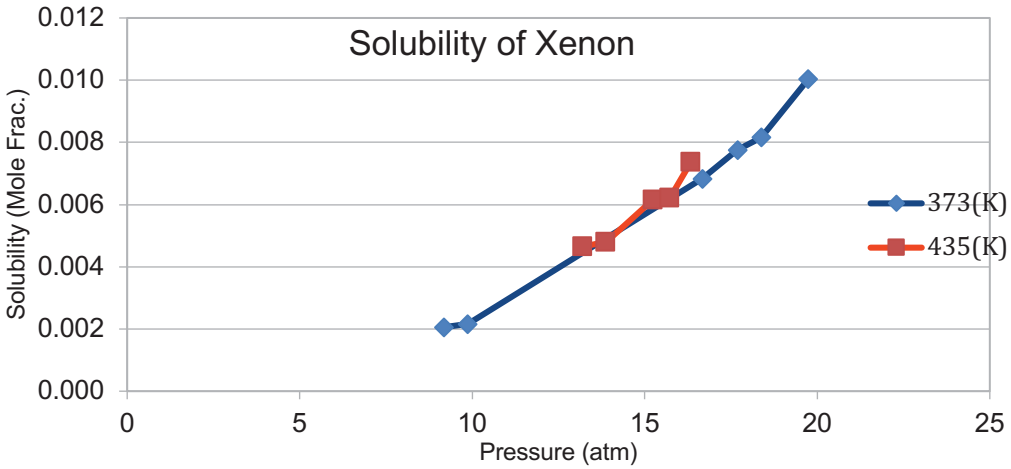

Figure 6 (Right) Solubility values for isothermal data series at the listed temperatures (±0.5K) of Xenon in aqueous solution

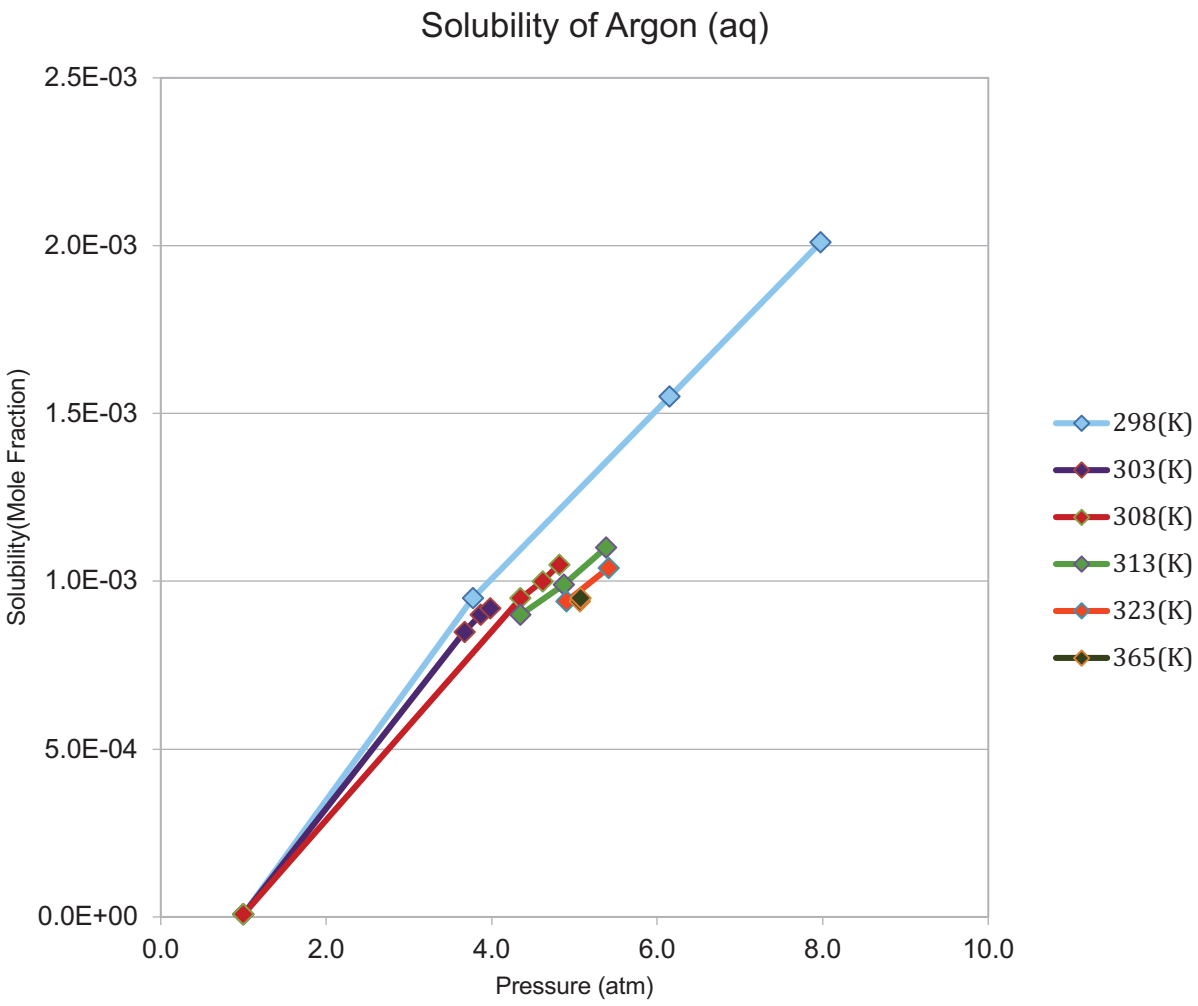

Figure 7 (Below) Solubility values for isothermal data series at the listed temperatures of Argon in aqueous solution. Argon had the most abundant amount of historical solubility data

Discussion

Pressure and Temperature

Although a limited amount of empirical data is available in the literature, the need for further experimental investigations is evident. Figure 6 displays two trends of xenon solubility data, within which a divergence is apparent. Making general assumptions of xenon characteristics based on this chart is impractical due to the limited amount of data points. However, Figure 6 provides a more detailed view, as the abundance of empirical argon solubility data was the greatest of all the noble gases. A gap between the temperature trends is greater than 19% for 365K and 303K temperature trends. In general, a limited amount of information exists for noble gas solubility. The range of pressures for which empirical data exists is at best only representative up to the first few hundred meters of burial (Crovetto et. al. 1981).

Impact of molecular weights

Figure 4 reveals an interesting trend in solubility with changes in temperature. Although the more massive noble gases (Xenon, Krypton, etc.) have a greater overall solubility, their change in solubility is orders of magnitude greater than the respective change in low molecular weight gases (Helium, Neon). Even though the limited temperature range of 288.15K – 308.15K, this could still be a valid representation of some groundwater system environments (Cey et. al. 2009). From interpretation of Figure 4, it appears that a strong relationship exists between molecular mass, low pressure/temperature solubility, and the rate of solubility change with increasing pressure and temperatures.

Implications for theoretical validation

Naturally occurring fluid systems are usually not pure solute and solvent mixtures, dissolved salts, gases, or even other fluids will disrupt anticipated patterns of behavior. It has been observed that if oil is added to a gas-water system, the relative abundancies of different noble gases dissolved in solution becomes more variable (Ballentine et. al. 2002). Several equations of state attempt to describe these fluctuations through the introduction of parameters to account for these deviations (Abudour et al. 2014). Utilization of a comprehensive empirical dataset to weigh theoretical predictions against may potentially increase accuracy in predicted phase equilibria.

CONCLUSIONS

This work makes steps toward understanding the phenomena of noble gas partitioning underground. Empirical solubility values for of ^{4}He, ^{20}Ne, ^{40}Ar, ^{84}Kr, and ^{132}Xe from peer reviewed, historical sources are collected and organized in Table A. The data are examined for trends by isolation of pressure and temperature parameters. At this junction, it is evident that the intrinsic molecular mass of a selected gas has an effect on the rate of change in solubility as temperature is increased or decreased. Furthermore, significant variation of solubility in several series of isothermal data across a range pressures is observed. Valid and practical explanation or modeling of subterranean fluid mechanics can be convoluted using current equations of state and predictive models. Further research into noble gas solubility, especially in systems involving multiphase or multicomponent flow, is sorely needed.

Recommendations for Future Work

Unfortunately, the sample size range for pressures in empirical solubility data was quite limited with 1≤100atm range. Economic petroleum reservoirs extend to depths of over of 10,000m below the Earth's surface (Selley & Sonnenberg 2015), and the corresponding hydrostatic pressure at this depth can exceed 1000atm of pressure. Further studies of pressures up to this range are warranted. Studying a more narrow range of temperatures reflecting expected underground gradient temperature ranges of ~285K-425K could prove practical. Studies involving solutes with dissolved salts, or multi-component mixtures with oil have potential to aid in creating a thorough picture of fluid interactions.

Overall, this area of study is unexplored, and surprisingly so considering the implications it has for several wealthy economic industries. A more refined knowledge of noble gas solubility will affect fluid mechanic modeling and overall resource viability and value. The potential for effective change by furthering the study of the phenomena is great.

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APPENDIX

Table A: Solubility of Select Gases in Aqueous Solution

Gas	Temp(K)	Pressure(atm)	Solubility (mole Fraction)	Source	Gas	Temp(K)	Pressure(atm)	Solubility (mole Fraction)	Source
He-4(aq)	288.15	1.0000	1.5100E-05	2	Kr-84(aq)	288.15	1.0000	5.6960E-05	2
	293.15	1.0000	1.4550E-05	2		293.15	1.0000	5.0410E-05	2
	298.15	1.0000	1.4110E-05	2		298.15	1.0000	4.5120E-05	2
	303.15	1.0000	1.3770E-05	2		303.15	1.0000	4.0790E-05	2
	308.15	1.0000	1.3500E-05	2		308.15	1.0000	3.7250E-05	2
	377.15	9.8560	1.0000E-03	3		333.70	23.5480	6.3320E-04	1
	422.56	8.0870	1.2000E-03	3		343.35	5.2010	1.4000E-03	3
	435.93	6.8046	5.9966E-03	5		359.00	23.9822	5.1400E-04	1
	435.93	13.6092	1.9664E-02	5		387.60	23.9329	4.9510E-04	1
	435.93	20.4138	3.7505E-02	5		426.00	24.9001	4.8650E-04	1
	523.78	4.5430	1.8000E-03	3		448.15	4.8200	1.2000E-03	3
	548.25	3.4120	1.9000E-03	3		448.15	4.3250	1.1500E-03	3
						477.50	31.7296	4.8280E-04	1
Ne-20(aq)	288.15	1.0000	7.1230E-06	2		523.40	66.1337	1.0752E-04	1
	293.15	1.0000	7.0440E-06	2		525.60	5.7410	2.4000E-03	3
	294.90	23.4000	1.9510E-04	1					
	298.15	1.0000	6.9970E-06	2	Xe-132(aq)	288.15	1.0000	1.0519E-04	2
	303.15	1.0000	6.9780E-06	2		293.15	1.0000	9.0510E-05	2
	308.15	1.0000	6.9870E-06	2		298.15	1.0000	7.8900E-05	2
	334.40	20.5675	1.5520E-04	1		303.15	1.0000	6.9610E-05	2
	343.20	11.7210	9.0000E-04	3		308.15	1.0000	6.2120E-05	2
	361.00	22.1466	1.7770E-04	1		334.50	19.5806	6.9720E-04	1
	388.90	22.0873	1.8600E-04	1		343.40	5.8750	1.9000E-03	3
	397.60	12.0220	1.0000E-03	3		364.10	21.0807	6.2080E-04	1
	427.70	21.5741	2.0350E-04	1		373.15	9.1862	2.0594E-03	4
	447.63	12.3540	1.2600E-03	3		373.15	9.8667	2.1620E-03	4
	499.55	11.4660	1.6000E-03	3		373.15	16.6713	6.8253E-03	4
	543.20	81.8061	8.4500E-04	1		373.15	17.6920	7.7568E-03	4
	543.40	80.8882	8.3860E-04	1		373.15	18.3724	8.1517E-03	4
	556.90	8.3200	2.0000E-03	3		373.15	19.7333	1.0024E-02	4
						391.50	20.8438	5.6680E-04	1
Ar-40(aq)	288.15	1.0000	8.7020E-05	2		398.68	4.4640	1.7000E-03	4
	293.15	1.0000	8.3950E-05	2		435.93	13.2009	4.6518E-03	4
	298.15	1.0000	8.1520E-06	2		435.93	13.8814	4.7892E-03	4
	298.16	6.1500	1.5500E-03	3		435.93	15.2423	6.1533E-03	4
	298.18	29.2880	7.3700E-03	3		435.93	15.7186	6.1978E-03	4
	298.25	7.9760	2.0100E-03	3		435.93	16.3310	7.3548E-03	4
	298.26	3.7730	9.5000E-04	3		439.30	21.8110	5.1860E-04	1
	303.15	1.0000	7.9660E-06	2		448.90	5.2650	2.1000E-03	3
	303.19	3.6690	8.5000E-04	3		473.70	53.5505	1.4767E-04	1
	303.24	3.8640	9.0000E-04	3		476.30	23.2618	2.7370E-04	1
	303.25	3.9850	9.2000E-04	3		498.28	3.9980	1.9500E-03	3
	306.90	22.1959	4.6670E-04	1		557.35	3.9240	3.0000E-03	3
	308.14	4.3470	9.5000E-04	3					
	308.15	4.8160	1.0500E-03	3	CH_4(aq)	288.15	1.0000	3.1220E-05	2
	308.15	1.0000	7.8290E-06	2		293.15	1.0000	2.8060E-05	2
	308.16	4.6130	1.0000E-03	3		297.50	18.3666	4.3510E-04	1
	313.14	5.3790	1.1000E-03	3		298.15	1.0000	2.5520E-05	2
	313.20	4.8680	9.9000E-04	3		303.15	1.0000	2.3460E-05	2
	313.22	4.3480	9.0000E-04	3		308.15	1.0000	2.1800E-05	2
	323.15	4.9030	9.4000E-04	3		333.70	13.0965	2.1240E-04	1
	323.16	5.4110	1.0400E-03	3		385.30	20.6464	2.9850E-04	1
	335.90	20.9820	3.4290E-03	1		388.40	21.2781	3.0850E-04	1
	338.25	5.0910	9.5000E-04	3		430.60	21.0313	3.0250E-04	1
	353.15	5.6270	1.0500E-03	3		473.20	31.6802	4.1460E-04	1
	364.26	5.0750	9.5000E-04	3		518.30	63.6664	1.0337E-03	1
	365.30	16.4816	2.4780E-04	1					
	365.50	5.0680	9.4000E-04	3					1 – Crovetto et. al. (1981)
	368.30	20.0642	2.3960E-04	1					2 – Gevantman
	397.30	43.7700	3.5790E-04	1					3 – Potter, Clyne (1978)
	398.85	5.6730	1.0700E-03	3					4 - Stephan et al (1956)
	399.03	5.2740	1.0000E-03	3					5 - Pray, Schweikert (1952)
	424.70	24.9297	3.7860E-04	1					
	453.70	21.8505	2.7310E-04	1					
	495.80	3.4690	9.1000E-04	3					
	506.55	5.1020	1.4000E-03	3					
	540.42	4.5740	1.8000E-03	3					
	561.12	3.9080	2.0900E-03	3					
	568.40	95.8401	9.5040E-04	1					